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Applicant : Shigeru YAMAGO et al

Serial No. : 10/554,242

For : PROCESS FOR PRODUCTION OF LIVING-RADICAL POLYMERS AND
POLYMERS

Hon. Commissioner of Patent and Trademarks

Washington, D.C. 20231

DECLARATION

Sir:

In the matter of Japanese Patent
Application No. 121,223/2003

I, Iwao Tamura, residing at c/o Tamura International Patent
Office, 9-22, Terauchi 1-chome, Toyonaka-shi, Osaka 561-0872, JAPAN,
who am a patent attorney solemnly and sincerely declare as follows:

1. That I understand well the Japanese and English languages.
2. That the document attached hereto is a full true and
faithful translation into English, made by me Iwao Tamura, of the
above Japanese patent application.
3. That I hereby declare that all statements made herein of
my own knowledge are true and that all statements made on
information and belief are believed to be true; and further that
these statements were made with the knowledge that willful false
statements and the like so made are punishable by fine or
imprisonment, or both, under Section 1001 of Title 18 of the United
States Code and that such willful false statements may jeopardize
the validity of the application or any patent issued thereon.

February 26, 2007

I. Tamura
Iwao Tamura



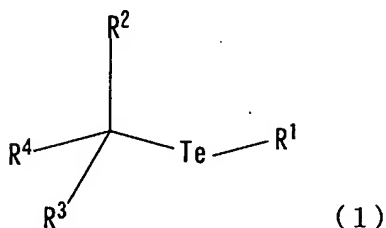
[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION]

PROCESS FOR THE PRODUCTION OF LIVING-RADICAL POLYMERS
AND POLYMERS

5 [CLAIMS]

1. A process for producing a living radical polymer characterized in that a vinyl monomer is polymerized with use of a living radical polymerization initiator represented by the formula (1), an azo type polymerization initiator and a
10 ditelluride compound represented by the formula (2)



wherein R^1 is C_1 - C_8 alkyl, aryl, substituted aryl or an aromatic heterocyclic group, R^2 and R^3 are each a hydrogen atom or C_1 - C_8 alkyl, and R^4 is aryl, substituted aryl, an
15 aromatic heterocyclic group, carbonyl, oxycarbonyl or cyano



wherein R^1 is the same as above.

2. A living radical polymer obtainable by polymerizing a vinyl monomer with use of a living radical polymerization
20 initiator represented by the formula (1), an azo type polymerization initiator and a ditelluride compound represented by the formula (2).

3. A mixture of a living radical polymerization

initiator represented by the formula (1), an azo type polymerization initiator and a ditelluride compound represented by the formula (2).

5 [DETAILED DESCRIPTION OF THE INVENTION]

[TECHNICAL FIELD]

The present invention relates to a process for producing living radical polymers and the living radical polymers obtained by the process.

10 [PRIOR ART]

Azo compounds are used as a radical polymerization initiator. Especially, AIBN (2,2'-azobis-isobutyronitrile) is an important compound and is widely used among azo-type radical polymerization initiators. In such reactions, the
15 azo-type initiator is used for polymerization of extremely various vinyl monomers such as styrene, alkyl (meth)acrylate, acrylonitrile or the like.

The above methods make it possible to polymerize various monomers, but are unsuited to precisely control
20 molecular weights and molecular weight distributions of the resulting polymers.

In order to solve the above problem, a process is known in which styrene is polymerized with use of AIBN and diphenyl ditelluride (DPDTe) to obtain polystyrene (see, eg., non-
25 patent literature 1).

[PROBLEM TO BE SOLVED BY THE INVENTION]

However, the above process discloses only an aromatic DPDTe as a ditelluride compound and only styrene as a vinyl

monomer, and produces a polymer having a molecular weight distribution ($PD=M_w/M_n$) of about 1.18 to about 1.26.

Accordingly, it is known from the above literature that a polymer having precision control of molecular weight

5 distribution ($PD=M_w/M_n$) can be obtained when styrene is used as a vinyl monomer, but there is no knowledge about a polymer when a monomer other than styrene is used. We have investigated a polymerization using a vinyl monomer other than styrene such as a (meth)acrylate ester, etc., and found
10 that a polymer having an excellent molecular weight distribution was not obtained.

[non-patent literature 1 : Polymer Bulletin 43, 143-150 (1999)]

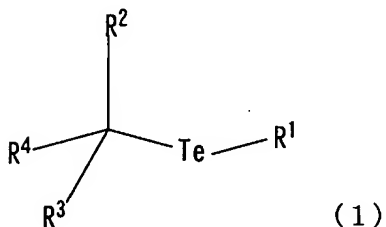
An object of the present invention is to provide a
15 process for producing a living radical polymer by polymerizing a vinyl monomer with use of a compound represented by the formula (1), an azo type polymerization initiator and a ditelluride compound represented by the formula (2), the process making possible to prepare living
20 radical polymers having more precise molecular weight and molecular weight distributions ($PD=M_w/M_n$) under mild conditions, even when not only styrene but a vinyl monomer other than styrene such as a (meth)acrylate ester, etc. is used; and the polymer.

25

[MEANS FOR SOLVING THE PROBLEM]

The present invention provides a process for producing a living radical polymer characterized in that a vinyl

monomer is polymerized with use of an organotellurium compound represented by the formula (1), an azo type polymerization initiator and a ditelluride compound represented by the formula (2), and the living radical
 5 polymer obtainable by the process

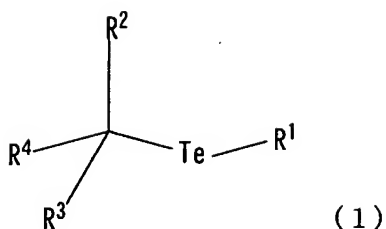


wherein R^1 is C_1 - C_8 alkyl, aryl, substituted aryl or an aromatic heterocyclic group, R^2 and R^3 are each a hydrogen atom or C_1 - C_8 alkyl, and R^4 is aryl, substituted aryl, an
 10 aromatic heterocyclic group, carbonyl, oxycarbonyl or cyano
 $(R^1Te)_2$ (2)

wherein R^1 is the same as above.

[EMBODIMENT OF PRACTICING THE INVENTION]

The living radical polymer of the present invention is
 15 produced by polymerizing a vinyl monomer in the presence of an organotellurium compound represented by the formula (1) and a compound represented by the formula (2) using an azo type polymerization initiator



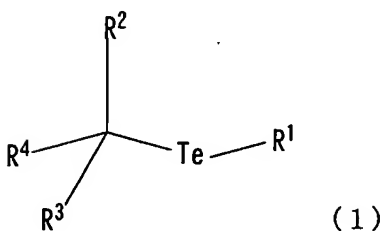
wherein R^1 is C_1 - C_8 alkyl, aryl, substituted aryl or an aromatic heterocyclic group, R^2 and R^3 are each a hydrogen atom or C_1 - C_8 alkyl, and R^4 is aryl, substituted aryl, an aromatic heterocyclic group, carbonyl, oxycarbonyl or cyano



wherein R^1 is the same as above.

The compounds of the formula (1) to be used in the present invention are as follows

10



wherein R^1 is C_1 - C_8 alkyl, aryl, substituted aryl or an aromatic heterocyclic group, R^2 and R^3 are each a hydrogen atom or C_1 - C_8 alkyl, and R^4 is aryl, substituted aryl, an aromatic heterocyclic group, carbonyl, oxycarbonyl or cyano.

15

Examples of groups represented by R^1 are as follows.

Examples of C_1 - C_8 alkyl groups usable are straight-chain, branched chain or cyclic alkyl groups having 1 to 8 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl,

cyclopropyl, n-butyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, n-hexyl, n-heptyl and n-octyl. Preferable alkyl groups are straight-chain or branched chain alkyl groups having 1 to 4 carbon atoms. Methyl, ethyl or butyl is more
5 preferable.

Examples of groups usable include aryl groups such as phenyl and naphthyl, substituted aryl groups such as phenyl having a substituent and naphthyl having a substituent, and aromatic heterocyclic groups such as pyridyl, furyl and
10 thienyl. Examples of substituents of aryl groups having a substituent are a halogen atom, hydroxyl, alkoxyl, amino, nitro, cyano, carbonyl-containing groups represented by $-\text{COR}^a$ ($R^a = \text{C}_1\text{-C}_8$ alkyl, aryl, $\text{C}_1\text{-C}_8$ alkoxyl or aryloxy), sulfonyl, trifluoromethyl, etc. Preferable aryl groups are phenyl and
15 trifluoromethyl-substituted phenyl. Preferably such substituted groups have one or two substituents at the para-position or ortho-position.

Examples of groups represented by R^2 and R^3 are as follows.

20 Examples of $\text{C}_1\text{-C}_8$ alkyl groups usable are the same as the alkyl groups represented by R^1 and given above.

Examples of groups represented by R^4 are as follows.

Examples of aryl, substituted aryl, aromatic heterocyclic groups usable are the same as those groups
25 represented by R^1 and given above.

Examples of preferred oxycarbonyl groups are those represented by $-\text{COOR}^b$ ($R^b = \text{H}, \text{C}_1\text{-C}_8$ alkyl or aryl) such as carboxyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl,

n-butoxycarbonyl, sec-butoxycarbonyl, tert-butoxycarbonyl, n-pentoxycarbonyl and phenoxycabonyl. Methoxycarbonyl and ethoxycarbonyl are more desirable oxycarbonyl groups.

5 Examples of organotellurium compounds represented by the formula (1) are as follows.

Such organotellurium compounds are (methyltellanyl-methyl)benzene, (1-methyltellanyl-ethyl)benzene, (2-methyltellanyl-propyl)benzene, 1-chloro-4-(methyltellanyl-methyl)benzene, 1-hydroxy-4-(methyltellanyl-methyl)benzene,
 10 1-methoxy-4-(methyltellanyl-methyl)benzene, 1-amino-4-(methyltellanyl-methyl)benzene, 1-nitro-4-(methyltellanyl-methyl)benzene, 1-cyano-4-(methyltellanyl-methyl)benzene, 1-methylcarbonyl-4-(methyltellanyl-methyl)benzene, 1-phenylcarbonyl-4-(methyltellanyl-methyl)benzene, 1-
 15 methoxycarbonyl-4-(methyltellanyl-methyl)benzene, 1-phenoxycarbonyl-4-(methyltellanyl-methyl)benzene, 1-sulfonyl-4-(methyltellanyl-methyl)benzene, 1-trifluoromethyl-4-(methyltellanyl-methyl)benzene, 1-chloro-4-(1-methyltellanyl-ethyl)benzene, 1-hydroxy-4-(1-methyltellanyl-ethyl)benzene,
 20 1-methoxy-4-(1-methyltellanyl-ethyl)benzene, 1-amino-4-(1-methyltellanyl-ethyl)benzene, 1-nitro-4-(1-methyltellanyl-ethyl)benzene, 1-cyano-4-(1-methyltellanyl-ethyl)benzene, 1-methylcarbonyl-4-(1-methyltellanyl-ethyl)benzene, 1-phenylcarbonyl-4-(1-methyltellanyl-ethyl)benzene, 1-
 25 methoxycarbonyl-4-(1-methyltellanyl-ethyl)benzene, 1-phenoxycarbonyl-4-(1-methyltellanyl-ethyl)benzene, 1-sulfonyl-4-(1-methyltellanyl-ethyl)benzene, 1-trifluoromethyl-4-(1-methyltellanyl-ethyl)benzene, 1-chloro-

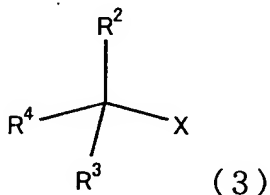
4-(2-methyltellanyl-ethyl)benzene, 1-hydroxy-4-(2-methyltellanyl-propyl)benzene, 1-methoxy-4-(2-methyltellanyl-propyl)benzene, 1-amino-4-(2-methyltellanyl-propyl)benzene, 1-nitro-4-(2-methyltellanyl-propyl)benzene, 1-cyano-4-(2-methyltellanyl-propyl)benzene, 1-methylcarbonyl-4-(2-methyltellanyl-propyl)benzene, 1-phenylcarbonyl-4-(2-methyltellanyl-propyl)benzene, 1-methoxycarbonyl-4-(2-methyltellanyl-propyl)benzene, 1-phenoxy carbonyl-4-(2-methyltellanyl-propyl)benzene, 1-sulfonyl-4-(2-methyltellanyl-propyl)benzene, 1-trifluoromethyl-4-(2-methyltellanyl-propyl)benzene, 2-(methyltellanyl-methyl)pyridine, 2-(1-methyltellanyl-ethyl)pyridine, 2-(2-methyltellanyl-propyl)pyridine, 2-methyl-2-methyltellanyl-propanal, 3-methyl-3-methyltellanyl-2-butanone, methyl 2-methyltellanyl-ethanate, methyl 2-methyltellanyl-propionate, methyl 2-methyltellanyl-2-methylpropionate, ethyl 2-methyltellanyl-ethanate, ethyl 2-methyltellanyl-propionate, ethyl 2-methyltellanyl-2-methylpropionate, 2-methyltellanylacetonitrile, 2-methyltellanyl-propionitrile, 2-methyl-2-methyltellanyl-propionitrile, (phenyltellanyl-methyl)benzene, (1-phenyltellanyl-ethyl)benzene, (2-phenyltellanyl-propyl)benzene, etc. The above compounds also include all compounds having ethyltellanyl, 1-ethyltellanyl, 2-ethyltellanyl, butyltellanyl, 1-butyltellanyl or 2-butyltellanyl, as changed from the portion of methyltellanyl, 1-methyltellanyl or 2-methyltellanyl.

Preferable are (methyltellanyl-methyl)benzene, (1-methyltellanyl-ethyl)benzene, (2-methyltellanyl-

propyl)benzene, methyl 2-methyltellanyl-2-methylpropionate,
 ethyl 2-methyltellanyl-2-methylpropionate, 2-methyltellanyl-
 propionitrile, 2-methyl-2-methyltellanylpropionitrile,
 (ethyltellanyl-methyl)benzene, (1-ethyltellanyl-
 5 ethyl)benzene, (2-ethyltellanyl-propyl)benzene, methyl 2-
 ethyltellanyl-2-methylpropionate, ethyl 2-ethyltellanyl-2-
 methylpropionate, 2-ethyltellanyl-propionitrile, 2-methyl-2-
 ethyltellanylpropionitrile, (n-butyltellanyl-methyl)benzene,
 (1-n-butyltellanyl-ethyl)benzene, (2-n-butyltellanyl-
 10 propyl)benzene, methyl 2-n-butyltellanyl-2-methylpropionate,
 ethyl 2-n-butyltellanyl-2-methylpropionate, 2-n-
 butyltellanyl-propionitrile, 2-methyl-2-n-butyltellanyl-
 propionitrile.

The living radical polymerization initiator represented
 15 by the formula (1) can be prepared by reacting a compound of
 the formula (3), a compound of the formula (4) and metallic
 tellurium.

Examples of compounds represented by the formula (3)
 are as follows



20 wherein R^2 , R^3 and R^4 are as defined above, and X is a halogen
 atom.

Examples of groups represented by R^2 , R^3 and R^4 are as
 given above.

Examples of groups represented by X can be a halogen

atom such as fluorine, chlorine, bromine or iodine. Chlorine and bromine are preferable.

Examples of compounds usable are benzyl chloride, benzyl bromide, 1-chloro-1-phenylethane, 1-bromo-1-phenylethane, 2-chloro-2-phenylpropane, 2-bromo-2-phenylpropane, p-chlorobenzyl chloride, p-hydroxybenzyl chloride, p-methoxybenzyl chloride, p-aminobenzyl chloride, p-nitrobenzyl chloride, p-cyanobenzyl chloride, p-methylcarbonylbenzyl chloride, phenylcarbonylbenzyl chloride, p-methoxycarbonylbenzyl chloride, p-phenoxy carbonylbenzyl chloride, p-sulfonylbenzyl chloride, p-trifluoromethylbenzyl chloride, 1-chloro-1-(p-chlorophenyl)ethane, 1-bromo-1-(p-chlorophenyl)ethane, 1-chloro-1-(p-hydroxyphenyl)ethane, 1-bromo-1-(p-hydroxyphenyl)-ethane, 1-chloro-1-(p-methoxyphenyl)ethane, 1-bromo-1-(p-methoxyphenyl)ethane, 1-chloro-1-(p-aminophenyl)ethane, 1-bromo-1-(p-aminophenyl)ethane, 1-chloro-1-(p-nitrophenyl)ethane, 1-bromo-1-(p-nitrophenyl)ethane, 1-chloro-1-(p-cyanophenyl)ethane, 1-bromo-1-(p-cyanophenyl)ethane, 1-chloro-1-(p-methylcarbonylphenyl)ethane, 1-bromo-1-(p-methylcarbonylphenyl)ethane, 1-chloro-1-(p-phenylcarbonylphenyl)ethane, 1-bromo-1-(p-phenylcarbonylphenyl)-ethane, 1-chloro-1-(p-methoxycarbonylphenyl)ethane, 1-bromo-1-(p-methoxycarbonylphenyl)ethane, 1-chloro-1-(p-phenoxy carbonylphenyl)-ethane, 1-bromo-1-(p-phenoxy carbonylphenyl)ethane, 1-chloro-1-(p-sulfonylphenyl)ethane, 1-bromo-1-(p-sulfonylphenyl)ethane, 1-

chloro-1-(p-trifluoromethylphenyl)ethane, 1-bromo-1-(p-trifluoromethylphenyl)ethane, 2-chloro-2-(p-chlorophenyl)propane, 2-bromo-2-(p-chlorophenyl)propane, 2-chloro-2-(p-hydroxyphenyl)-propane, 2-bromo-2-(p-hydroxyphenyl)propane, 2-chloro-2-(p-methoxyphenyl)propane, 2-bromo-2-(p-methoxyphenyl)propane, 2-chloro-2-(p-aminophenyl)propane, 2-bromo-2-(p-aminophenyl)propane, 2-chloro-2-(p-nitrophenyl)propane, 2-bromo-2-(p-nitrophenyl)-propane, 2-chloro-2-(p-cyanophenyl)propane, 2-bromo-2-(p-cyanophenyl)propane, 2-chloro-2-(p-methylcarbonylphenyl)propane, 2-bromo-2-(p-methylcarbonylphenyl)propane, 2-chloro-2-(p-phenylcarbonylphenyl)propane, 2-bromo-2-(p-phenylcarbonylphenyl)-propane, 2-chloro-2-(p-methoxycarbonylphenyl)propane, 2-bromo-2-(p-methoxycarbonylphenyl)propane, 2-chloro-1-(p-phenoxy carbonylphenyl)propane, 2-bromo-2-(p-phenoxy carbonylphenyl)propane, 2-chloro-2-(p-sulfonylphenyl)propane, 2-bromo-2-(p-sulfonylphenyl)propane, 2-chloro-2-(p-trifluoromethylphenyl)propane, 2-bromo-2-(p-trifluoromethylphenyl)propane, 2-(chloromethyl)pyridine, 2-(bromomethyl)pyridine, 2-(1-chloroethyl)pyridine, 2-(1-bromoethyl)pyridine, 2-(2-chloropropyl)pyridine, 2-(2-bromopropyl)pyridine, methyl 2-chloroethanoate, methyl 2-bromoethanoate, methyl 2-chloropropionate, methyl 2-bromoethanoate, methyl 2-chloro-2-methylpropionate, methyl 2-bromo-2-methylpropionate, ethyl 2-chloroethanoate, ethyl 2-bromoethanoate, ethyl 2-chloropropionate, ethyl 2-

bromoethanoate, ethyl 2-chloro-2-ethylpropionate, ethyl 2-bromo-2-ethylpropionate, 2-chloroacetonitrile, 2-bromoacetonitrile, 2-chloropropionitrile, 2-bromopropionitrile, 2-chloro-2-methylpropionitrile, 2-bromo-
 5 2-methylpropionitrile, etc.

Examples of compounds represented by the formula (4) are as follows.



wherein R^1 is as defined above, M is an alkali metal, alkaline
 10 earth metal or copper atom, and m is 1 when M is an alkali metal, m is 2 when M is an alkaline earth metal, or m is 1 or 2 when M is a copper atom.

Examples of groups represented by R^1 are as given above.

Examples of metals represented by M are lithium,
 15 sodium, potassium and like alkali metals, magnesium, calcium and like alkaline earth metals, and copper. Lithium is desirable.

In case that M is magnesium, the compound (4) may either be $Mg(R^1)_2$ or a compound represented by MgX (X is a
 20 halogen atom) which is a Grignard reagent. Chlorine and bromine are preferable.

Examples of compounds usable are methyllithium, ethyllithium, n-butyllithium, phenyllithium, p-methoxyphenyllithium, etc. Methyllithium, ethyllithium, n-butyllithium and
 25 phenyllithium are preferable.

Next, a detailed description will be given of the process for preparing the compound.

Metallic tellurium is suspended in a solvent. Examples

of solvents usable are tetrahydrofuran (THF) and like polar solvents, toluene, xylene and like aromatic solvents, hexane and like aliphatic hydrocarbons, dialkyl ethers and like ethers, etc. THF is preferable. The amount of solvent to be
5 used, which is suitably adjusted, is 1 to 100 ml, preferably 5 to 20 ml, per gram of metallic tellurium.

A compound (4) is slowly added dropwise to the suspension, followed by stirring. The reaction time differs with the reaction temperature and pressure and is usually 5
10 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is -20°C to 80°C , preferably 15°C to 40°C , more preferably room temperature. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum.

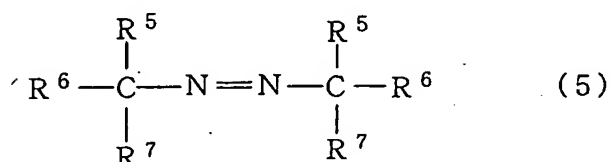
15 Next, a compound (3) is added to the reaction mixture, followed by stirring. The reaction time differs with the reaction temperature and pressure and is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction
20 temperature is -20°C to 80°C , preferably 15°C to 40°C , more preferably room temperature. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum.

The proportions of the compound (3) and compound (4) to metallic tellurium are 0.5 to 1.5 moles of the compound (3)
25 and 0.5 to 1.5 moles of the compound (4), preferably 0.8 to 1.2 moles of the compound (3) and 0.8 to 1.2 moles of the compound (4), per mole of metallic tellurium.

After the completion of the reaction, the solvent is

concentrated, and the desired compound is isolated and purified. Although the method of purification can be determined suitably depending on the compound, usually vacuum distillation or recrystallization is preferable.

5 An azo type polymerization initiator used in the present invention are not particularly limited insofar as it is usable in a usual radical polymerization. Example thereof are those represented by the formula (5)



wherein R^5 and R^6 are same or different and are each $\text{C}_1\text{-C}_{10}$ alkyl, carboxyl-substituted $\text{C}_1\text{-C}_4$ alkyl, phenyl having or not having a substituent, and may form an alicyclic ring together with a carbon atom, R^7 is cyano, acetoxy, carbamoyl or $(\text{C}_1\text{-C}_4 \text{ alkoxy})\text{carbonyl}$.

15 In the azo type compound of the formula (5) usable in the present invention, examples of $\text{C}_1\text{-C}_{10}$ alkyl groups in R^5 and R^6 are methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, etc. Examples of $\text{C}_1\text{-C}_4$ alkyl groups in carboxyl-substituted $\text{C}_1\text{-C}_4$ alkyl are methyl, ethyl, propyl, isopropyl, butyl, etc. Examples of alicyclic rings formed by R^5 and R^6 together with a carbon atom are

20 cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, etc. Phenyl may have substituent such as hydroxyl, methyl, ethyl, methoxy, ethoxy, nitro, amino, acetyl, acetylamino, etc. Examples of $(\text{C}_1\text{-C}_4 \text{ alkoxy})\text{carbonyl}$ in R^7 are methoxycarbonyl,

ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, butoxycarbonyl, etc.

Examples of the azo type compound of the formula (5) are 2,2'-azobis(isobutyronitrile) (AIBN), 2,2'-azobis(2-methylbutyronitrile) (AMBN), 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN), 1,1'-azobis(1-cyclohexanecarbonitrile) (ACHN), dimethyl-2,2'-azobisisobutyrate (MAIB), 4,4'-azobis(4-cyanovaleric acid) (ACVA), 1,1'-azobis(1-acetoxy-1-phenylethane), 2,2'-azobis(2-methylbutylamide) and 1,1'-azobis(methyl 1-cyclohexanecarbonate).

Examples of compounds represented by the formula (2) and useful for the present invention are as follows



wherein R^1 is the same as above.

The groups R^1 is the same as shown above.

More specific examples of compounds represented by the formula (2) are dimethyl ditelluride, diethyl ditelluride, di-n-propyl ditelluride, diisopropyl ditelluride, dicyclopropyl ditelluride, di-n-butyl ditelluride, di-sec-butyl ditelluride, di-tert-butyl ditelluride, dicyclobutyl ditelluride, diphenyl ditelluride, bis(p-methoxyphenyl) ditelluride, bis(p-aminophenyl) ditelluride, bis(p-nitrophenyl) ditelluride, bis(p-cyanophenyl) ditelluride, bis(p-sulfonylphenyl) ditelluride, dinaphthyl ditelluride, dipyridyl ditelluride, etc.

Such compounds are prepared, for example, by reacting metallic tellurium with a compound represented by the formula

(4) .

Metallic tellurium is suspended in a solvent. Examples of solvents usable are dimethylformamide (DMF), tetrahydrofuran (THF) and like polar solvents, toluene, xylene and like aromatic solvents, hexane and like aliphatic hydrocarbons, dialkyl ethers and like ethers. THF is preferable among these. The organic solvent is used usually in an amount of 5 to 10 ml, preferably 7 to 8 ml, per gram of metallic tellurium although the amount is suitably adjustable.

The compound represented by the formula (4) is slowly added dropwise to the suspension, followed by stirring. The reaction time is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours, although varying with the reaction temperature and pressure. The reaction temperature is -20°C to 80°C , preferably 15°C to 40°C , more preferably room temperature. The reaction is conducted usually at atmospheric pressure, but an increased or reduced pressure is usable.

Subsequently, water (which may be neutral water such as saline solution, alkali water such as aqueous solution of ammonium chloride, or acid water such as aqueous solution of hydrochloric acid) is added to the reaction mixture, followed by stirring. Although varying with the reaction temperature or pressure, the reaction time is usually 5 minutes to 24 hours, preferably 10 minutes to 2 hours. The reaction temperature is -20°C to 80°C , preferably 15°C to 40°C , more preferably room temperature. The reaction is conducted usually at atmospheric pressure, but an increased or reduced pressure is usable.

Metallic tellurium and the compound of the formula (4) are used in such a ratio that 0.5 to 1.5 moles, preferably 0.8 to 1.2 moles, of the compound of the formula (4) is used per mole of metallic tellurium.

5 After the completion of the reaction, the solvent is concentrated, and the desired product is isolated from the concentrate and purified. Although the compound can be purified by a suitably selected method, vacuum distillation or reprecipitation purification is usually desirable.

10 The vinyl monomer to be used in the present invention is not particularly limited insofar as the monomer can be subjected to radical polymerization. Examples of vinyl monomers usable are methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 15 octyl (meth)acrylate, lauryl (meth)acrylate and like (meth)acrylic acid esters, cyclohexyl (meth)acrylate, methylcyclohexyl (meth)acrylate, isobornyl (meth)acrylate, cyclododecyl (meth)acrylate and like cycloalkyl-containing unsaturated monomers, (meth)acrylic acid, maleic acid, 20 fumaric acid, itaconic acid, citraconic acid, crontonic acid, maleic anhydride and like carboxyl-containing unsaturated monomers, N,N-dimethylaminopropyl(meth)acrylamide, N,N-dimethylaminoethyl(meth)acrylamide, 2-(dimethylamino)ethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate and 25 like unsaturated monomers containing a tertiary amine, N-2-hydroxy-3-acryloyloxypropyl-N,N,N-trimethylammonium chloride, N-methacryloylaminoethyl-N,N,N-dimethylbenzylammonium chloride and like unsaturated monomers containing quaternary

ammonium base, glycidyl (meth)acrylate and like epoxy-
 containing unsaturated monomers, styrene, α -methylstyrene, 4-
 methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-
 methoxystyrene, 2-hydroxymethylstyrene, 2-chlorostyrene, 4-
 5 chlorostyrene, 2,4-dichlorostyrene, 1-vinylnaphthalene,
 divinylbenzene, p-styrenesulfonic acid or an alkali metal
 salt thereof (sodium salt or potassium salt, etc.) and like
 aromatic unsaturated monomers, 2-vinylthiophene, N-methyl-2-
 vinylpyrrole and like unsaturated monomers containing a
 10 heterocyclic ring, N-vinylformaldehyde, N-vinylacetamide and
 like vinylamides, 1-hexene, 1-octene, 1-decene and like α -
 olefins, butadiene, isoprene, 4-methyl-1,4-hexadiene, 7-
 methyl-1,6-octadiene and like dienes, vinyl acetate,
 hydroxyethyl methacrylate, acrylonitrile, acrylamide, N-
 15 isopropylacrylamide, N,N-dimethylacrylamide vinyl chloride,
 etc.

Preferable among these are (meth)acrylic acid ester,
 unsaturated monomers containing a tertiary amino group,
 styrene type monomers, acrylamide and N,N-dimethylacrylamide.

20 Examples of preferable (meth)acrylic acid ester
 monomers are methyl (meth)acrylate, ethyl (meth)acrylate,
 propyl (meth)acrylate and butyl (meth)acrylate.

Examples of preferable unsaturated monomers containing
 a tertiary amino group are N,N-dimethylaminoethyl-
 25 (meth)acrylamide and 2-(dimethylamino)ethyl (meth)acrylate.

Examples of preferable styrene type monomers are
 styrene, α -methylstyrene, o-methylstyrene, p-methylstyrene,
 p-methoxystyrene, p-t-butylstyrene, p-n-butylstyrene, p-

chlorostyrene, and p-styrenesulfonic acid or an alkali metal salt thereof (sodium salt or potassium salt, etc.). More preferable are styrene, p-methoxystyrene and p-chlorostyrene.

The term "(meth)acrylic acid" refers collectively to
5 "acrylic acid" and "methacrylic acid."

Among these preferable are methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate and butyl (meth)acrylate. Especially preferable are methyl (meth)acrylate and butyl (meth)acrylate, and most preferable
10 is methyl methacrylate.

Specifically stated, the living radical polymer of the present invention is produced by the process to be described below.

A vinyl monomer, an organotellurium compound
15 represented by the formula (1), an azo type polymerization initiator and a compound represented by the formula (2) are mixed together in a container having its inside air replaced by an inert gas. Next, the mixture is then stirred. The reaction temperature and the reaction time may be adjusted
20 suitably. The mixture is stirred usually at 40 to 150°C for 0.5 to 100 hours, preferably at 60 to 100°C for 1 to 30 hours. The reaction is conducted usually under atmospheric pressure, but may be conducted at increased pressure or in a vacuum. Examples of inert gases usable at this time are
25 nitrogen, argon, helium, etc., among which argon and nitrogen are preferred. Nitrogen is especially preferred.

Although the vinyl monomer and the compound represented by the formula (1) are used in amounts which are suitably

adjusted depending on the molecular weight and molecular weight distribution of the living radical polymer to be obtained, usually 5 to 10,000 moles, preferably 50 to 5,000 moles, of the vinyl monomer is used per mole of the compound
5 represented by the formula (1).

The compound represented by the formula (1) and the azo type polymerization initiator are used in the ratio of usually 0.01 to 100 moles, preferably 0.1 to 10 moles, especially preferably 0.1 to 5 moles, of the azo type
10 polymerization initiator per mole of the compound of the formula (1).

The compound represented by the formula (1) and the a compound represented by the formula (2) are used in the ratio of usually 0.1 to 100 moles, preferably 0.1 to 10 moles,
15 especially preferably 0.1 to 5 moles, of the a compound represented by the formula (2) per mole of the compound of the formula (1).

The polymerization reaction is conducted usually in the absence of solvent, while an organic solvent generally in use
20 for radical polymerization or an aqueous solvent may be used. Examples of organic solvents usable are benzene, toluene, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, chloroform, carbon tetrachloride, tetrahydrofuran (THF), ethyl acetate, trifluoromethylbenzene, etc. Examples
25 of aqueous solvents are water, methanol, ethanol, isopropanol, n-butanol, ethyl cellosolve, butyl cellosolve, 1-methoxy-2-propanol, etc. The amount of the solvent to be used is adjusted suitably. For example, 0.01 to 50 ml, preferably

0.05 to 5 ml, of the solvent is used per gram of the vinyl monomer.

After the completion of the reaction, the solvent used and the remaining monomer are removed in a vacuum to take out
5 the desired polymer, or the desired product is isolated by re-precipitation using a solvent wherein the product is insoluble. The reaction mixture can be treated by any method insofar as it causes no problem to the desired product.

The living radical polymerization initiator of the
10 present invention is adapted for excellent control of molecular weights and molecular weight distributions under very mild conditions.

The living radical polymer to be obtained by the invention is adjustable in molecular weight according to the
15 reaction time and the amount of the organotellurium compound, and can be 500 to 1,000,000 in number average molecular weight. The invention is especially suitable for producing living radical polymers having a number average molecular weight of 1,000 to 50,000.

20 The living radical polymer to be obtained by the invention is controlled to 1.05 to 1.50 in molecular weight distribution ($PD = M_w/M_n$). The molecular weight distribution is controllable to a narrower range of 1.05 to 1.30, a further narrower range of 1.10 to 1.20, a still narrower
25 range of 1.09 to 1.20, 1.09 to 1.17, 1.09 to 1.12.

It has been found that the living radical polymer of the present invention has a terminal group which is an alkyl, aryl, substituted aryl, aromatic heterocyclic group,

oxycarbonyl or cyano derived from the organotellurium compound and a growth terminal which is highly reactive tellurium. Accordingly, the organotellurium compound used for radical polymerization makes it easier to convert the
5 terminal group to other functional group than in the case of the living radical polymer obtained by conventional living radical polymerization. The living radical polymer obtained according to the invention is therefore usable as a macro living radical polymerization initiator (macroinitiator).

10 A-B diblock copolymers such as methyl methacrylate-styrene can be obtained using a macro living radical polymerization initiator of the invention. A-B-A triblock copolymers such as methyl methacrylate-styrene-methyl methacrylate and A-B-C triblock copolymers such as methyl
15 methacrylate-styrene-butyl acrylate are also available. This is attributable to the fact that the vinyl monomers of various different types are controllable by the living radical polymerization initiator and the ditelluride compound of the invention, and also to the fact that highly reactive
20 tellurium is present at the growth terminal of the living radical polymer obtained with use of the living radical polymerization initiator.

Stated more specifically, block copolymers are prepared by the processes to be described below.

25 For preparing A-B diblock copolymers such as methyl methacrylate-styrene copolymer, methyl methacrylate, an azo type polymerization initiator and compound of the formula (2) are mixed together first as in the process described above

for preparing a living radical polymer to obtain poly(methyl methacrylate), and subsequently mixing styrene with the polymer to obtain methyl methacrylate-styrene copolymer.

A-B-A triblock copolymers and A-B-C triblock copolymers
5 can be produced, for example, by preparing an A-B diblock copolymer by the above process and thereafter mixing a vinyl monomer (A) or vinyl monomer (C) with the copolymer to obtain the A-B-A or A-B-C triblock copolymer.

The preparation of each block may be followed directly
10 by the subsequent reaction for the next block, or the subsequent reaction for the next block may be initiated after the purification of the product resulting from the completion of the first reaction. The block copolymer can be isolated by a usual method.

15

[EXAMPLES]

The present invention will be described below in detail with reference to Examples, but is not limited thereto in any way. In Examples and Comparative Examples, properties were
20 determined by the following methods.

(1) Identification of ditelluride compound and living radical polymers

The ditelluride compound were identified based on the results of ^1H -NMR and MS analyses. The molecular weight and
25 molecular weight distribution of the living radical polymer were determined using GPC (gel permeation chromatography). The measuring instruments used are as follows.

^1H -NMR : Varian Gemini 2000 (300MHz for ^1H), JEOL JNM-A400

(400MHz for ^1H)

MS(HRMS) : JEOL JMS-300

Molecular weight and molecular weight distribution : liquid chromatography Shimadzu LC-10 [column : Shodex K-804L + K-

5 805L, polystyrene standard : TOSOH TSK Standard, poly(methyl methacrylate) standard : Shodex Standard M-75]

Preparation Example 1

Preparation of (2-methyl-2-methyltellanyl-propionitrile)

A 6.38 g quantity (50 mmoles) of metallic tellurium
 10 [product of Aldrich, brand name: Tellurium (-40 mesh)] was suspended in 50 ml of THF, and 52.9 ml (1.04 M diethyl ether solution, 55 mmoles) of methyllithium (product of Kanto Chemical Co., Ltd., diethyl ether solution) was slowly added dropwise to the suspension at room temperature (for 10
 15 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 20 minutes). To the reaction mixture was added 10.4 g (70 mmoles) of 2-bromo-2-methyl-propionitrile at room temperature, followed by stirring for 2 hours. After the completion of reaction, the
 20 solvent was concentrated in a vacuum, followed by vacuum distillation to give 4.10 g of red oil (39% in yield).

IR, HRMS, ^1H -NMR and ^{13}C -NMR analyses indicated that the product was 2-methyl-2-methyltellanyl-propionitrile.

IR(neat, cm^{-1}) 2217, 1713, 1458, 1370, 1225, 1117, 835

25 HRMS(EI) m/z: Calcd for $\text{C}_5\text{H}_9\text{NTe}(\text{M})^+$, 212.9797; Found 212.9799

^1H -NMR (300MHz, CDCl_3) 1.91(s, 6H), 2.38(s, 3H, TeCH_3)

^{13}C -NMR (75MHz, CDCl_3) -15.5, 2.2, 30.3, 125.1

Preparation Example 2

Preparation of ethyl-2-methyl-2-methyltellanyl-propionate

A 6.38 g quantity (50 mmoles) of metallic tellurium (same as above) was suspended in 50 ml of THF, and 52.9 ml (1.04 M diethyl ether solution, 55 mmoles) of methyllithium (same as above) was slowly added dropwise to the suspension at room temperature (for 10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (for 20 minutes). To the reaction mixture was added 10.7 g (55 mmoles) of ethyl-2-bromo-isobutyrate at room temperature, followed by stirring for 2 hours. After the completion of reaction, the solvent was concentrated in a vacuum, followed by vacuum distillation to give 6.53 g of yellow oil (51% in yield).

IR, HRMS, ^1H -NMR and ^{13}C -NMR analyses indicated that the product was ethyl-2-methyl-2-methyltellanyl-propionate. IR(neat, cm^{-1}) 1700, 1466, 1385, 1296, 1146, 1111, 1028
HRMS(EI) m/z: Calcd for $\text{C}_7\text{H}_{14}\text{O}_2\text{Te}(\text{M})^+$, 260.0056; Found 260.0053
 ^1H -NMR (300MHz, CDCl_3) 1.27(t, $J=6.9\text{Hz}$, 3H), 1.74(s, 6H), 2.15(s, 3H, TeCH_3), 4.16(q, $J=7.2\text{Hz}$, 2H)
 ^{13}C -NMR (75MHz, CDCl_3) -17.38, 13.89, 23.42, 27.93, 60.80, 176.75

Preparation Example 3

Preparation of ethyl-2-methyl-2-n-butyrtellanyl-propionate

A 6.38 g quantity (50 mmoles) of metallic tellurium (same as above) was suspended in 50 ml of THF, and 34.4 ml (55 mmoles) of n-butyllithium (product of Aldrich, 1.6 M hexane solution) was slowly added dropwise to the suspension at room temperature (for 10 minutes). The reaction mixture was

stirred until the metallic tellurium disappeared completely (for 20 minutes). To the reaction mixture was added 10.7 g (55 mmoles) of ethyl-2-bromo-isobutyrate at room temperature, followed by stirring for 2 hours. After the completion of
 5 reaction, the solvent was concentrated in a vacuum, followed by vacuum distillation to give 8.98 g of yellow oil (59.5% in yield).

¹H-NMR analysis indicated that the product was ethyl-2-methyl-2-n-butyltellanyl-propionate.

10 ¹H-NMR (300MHz, CDCl₃) 0.93(t, J=7.5Hz, 3H), 1.25(t, J=7.2Hz, 3H), 1.37(m, 2H), 1.74(s, 6H), 1.76(m, 2H), 2.90(t, J=7.5Hz, 2H, CH₂Te), 4.14(q, J=7.2Hz, 2H)

Preparation Example 4 (dimethyl ditelluride)

A 3.19 g quantity (25 mmoles) of metallic tellurium
 15 [product of Aldrich, brand name: Tellurium (-40 mesh)] was suspended in 25 ml of THF, and 25 ml (28.5 mmoles) of methyllithium [product of Kanto Chemical Co, Ltd., diethyl ether solution] was added slowly to the suspension at 0° C (10 minutes). The reaction mixture was stirred until the metallic
 20 tellurium disappeared completely (10 minutes). To the resulting reaction mixture was added 20 ml of a solution of ammonium chloride at room temperature, followed by stirring for 1 hour. The organic layer was separated off, and the aqueous layer was subjected to extraction with diethyl ether
 25 3 times. The organic layers were collected, dried over anhydrous sodium sulfate and concentrated in a vacuum, affording 2.69 g (9.4 mmoles, yield 75%) of blackish purple oil.

The product was found to be dimethyl ditelluride by MS (HRMS) and ^1H -NMR.

HRMS(EI) m/z: Calcd for $\text{C}_2\text{H}_6\text{Te}_2(\text{M})^+$, 289.8594; Found 289.8593

5 ^1H -NMR (300MHz, CDCl_3) 2.67(s, 6H)

Preparation Example 5 (di-n-butyl ditelluride)

A 3.19 g quantity (25 mmoles) of metallic tellurium (same as above) was suspended in 25 ml of THF, and 17.2 ml (27.5 mmoles) of n-butyllithium [product of Aldrich, 1.6 M
10 hexane solution] was added slowly to the suspension at 0°C (10 minutes). The reaction mixture was stirred until the metallic tellurium disappeared completely (10 minutes). To the resulting reaction mixture was added 20 ml of a solution of ammonium chloride at room temperature, followed by
15 stirring for 1 hour. The organic layer was separated off, and the aqueous layer was subjected to extraction with diethyl ether 3 times. The organic layers were collected, dried over anhydrous sodium sulfate and concentrated in a vacuum, affording 4.41 g (11.93 mmoles, yield 95%) of blackish purple
20 oil.

The product was found to be di-n-ditelluride by ^1H -NMR.

^1H -NMR(300MHz, CDCl_3) 0.93 (t, $J=7.3\text{Hz}$, 3H), 1.39(m, 2H), 1.71(m, 2H), 3.11(t, $J=7.6$, 2H, CH_2Te)

Reference Example 1

25 2-Bromo-2-methyl-propionitrile which was used in Preparation Example 1 was prepared as follows.

Bromine was slowly added dropwise to a solution of isobutyronitrile (200 mmoles) and phosphorus tribromide (PBr_3 ,

20 mmoles) in ether (Et_2O , 100 ml) in a reaction vessel while cooling with an ice-bath. After completion of dropwise addition, the mixture was reacted at room temperature for 14 hours. The resulting solution was poured into ice-water for work up, extracted with ether (three times), dried with magnesium sulfate, filtered to remove magnesium sulfate. The filtrate was concentrated by removing solvent by an evaporator. The resulting concentrate was purified by distillation, giving 17.08 g of colorless transparent liquid (b.p. 57°C / 43 mmHg) in 58 % yield.

Example 1

Along with 1.001 g (10 mmoles) of methyl methacrylate [stabilized with hydroquinone (HQ)], 21.1 mg (0.10 mmole) of the compound prepared in Preparation Example 1, 16.4 mg (0.10 mmole) of AIBN (Otsuka Chemical Co., Ltd., brand name:AIBN) and 28.5 mg (0.10 mmole) of the compound prepared in Preparation Example 4 were placed into a glove box with the inside air replaced by nitrogen, followed by stirring at 60°C for 2 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 200 ml of hexane which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried at room temperature to obtain 0.977 g of poly(methyl methacrylate).

Table 1 shows the result of GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)].

Comparative Example 1

Along with AIBN (same as above) (0.10 mmole), the compound prepared in Preparation Example 4 (0.10 mmole) and methyl methacrylate (same as above) (10 mmoles) were placed into a glove box with the inside air replaced by nitrogen, followed by stirring at 80 °C for 4 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 200 ml of hexane which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried at room temperature to obtain poly(methyl methacrylate).

Table 1 shows the result of GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)].

Table 1

	<u>reaction condition</u>	<u>yield (%)</u>	<u>Mn</u>	<u>PD</u>
Ex.1	60 °C, 2 hr	98	9600	1.15
Com.Ex.1	80 °C, 4 hr	98	16300	2.10

A comparison between Example 1 and Comparative Example 1 indicates that when the compound of the formula (1) was used, a living radical polymer of narrower molecular weight distribution (PD value closer to 1) is obtained.

Example 2

Along with 1.04 g (10 mmoles) of styrene, 21.1 mg (0.10 mmole) of the compound prepared in Preparation Example 1,

16.4 mg (0.10 mmole) of AIBN (same as above) and 28.5 mg (0.10 mmole) of the compound prepared in Preparation Example 4 were placed into a glove box with the inside air replaced by nitrogen, followed by stirring at 60 °C for 11 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 200 ml of methanol which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried at room temperature to obtain polystyrene (yield 57%).

GPC analysis (with reference to the molecular weight of an authentic sample of polystyrene) revealed Mn 6200 and PD=1.17.

Example 3

Along with 1.28 g (10 mmoles) of n-butyl acrylate (stabilized with hydroquinone), 21.1 mg (0.10 mmole) of the compound prepared in Preparation Example 1, 16.4 mg (0.10 mmole) of AIBN (same as above) and 28.5 mg (0.10 mmole) of the compound prepared in Preparation Example 4 were placed into a glove box with the inside air replaced by nitrogen, followed by stirring at 60 °C for 24 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 200 ml of hexane which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried at room temperature to obtain poly(n-butyl acrylate) (yield 14%).

GPC analysis [with reference to the molecular weight of

an authentic sample of poly(methyl methacrylate)] revealed Mn 1800 and PD=1.12.

Example 4

Along with 1.301 g (10 mmoles) of 2-hydroxyethyl
5 methacrylate, 21.1 mg (0.10 mmole) of the compound prepared
in Preparation Example 1, 16.4 mg (0.10 mmole) of AIBN (same
as above), 28.5 mg (0.10 mmole) of the compound prepared in
Preparation Example 4 and 1 ml of DMF were placed into a
glove box with the inside air replaced by nitrogen, followed
10 by stirring at 60 °C for 2 hours. After the completion of the
reaction, solvent and the remaining monomer were removed at
60 to 80 °C for 12 hours under the decompression (<0.1 mmHg).
The resulting polymer precipitate was collected by suction
filtration and dried to obtain 1.168 g of poly(2-hydroxyethyl
15 methacrylate) (yield 90%).

GPC analysis [with reference to the molecular weight of
an authentic sample of poly(methyl methacrylate)] revealed Mn
22300 and PD=1.18.

Example 5

20 Along with 1.001 g (10 mmoles) of methyl methacrylate
(same as above), 26.0 mg (0.10 mmole) of the compound
prepared in Preparation Example 2, 8.2 mg (0.05 mmole) of
AIBN (same as above) and 14.3 mg (0.05 mmole) of the compound
prepared in Preparation Example 4 were placed into a glove
25 box with the inside air replaced by nitrogen, followed by
stirring at 60 °C for 2 hours. After the completion of the
reaction, the reaction mixture was dissolved in 5 ml of
chloroform, and the solution was then poured into 200 ml of

hexane which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried at room temperature to obtain poly(methyl methacrylate) (yield 59.7%).

5 GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn 12000 and PD=1.09.

Example 6

Along with 1.001 g (10 mmoles) of methyl methacrylate
10 (same as above), 26.0 mg (0.10 mmole) of the compound prepared in Preparation Example 2, 8.2 mg (0.05 mmole) of AIBN (same as above) and 18.5 mg (0.05 mmole) of the compound prepared in Preparation Example 5 were placed into a glove box with the inside air replaced by nitrogen, followed by
15 stirring at 60 °C for 2 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 200 ml of hexane which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried at
20 room temperature to obtain poly(methyl methacrylate) (yield 41.3%).

GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed Mn 12000 and PD=1.10.

25 Example 7

Along with 1.001 g (10 mmoles) of methyl methacrylate (same as above), 30.18 mg (0.10 mmole) of the compound prepared in Preparation Example 3, 8.2 mg (0.05 mmole) of

AIBN (same as above) and 14.3 mg (0.05 mmole) of the compound prepared in Preparation Example 4 were placed into a glove box with the inside air replaced by nitrogen, followed by stirring at 60 °C for 2 hours. After the completion of the
5 reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 200 ml of hexane which was being stirred. The resulting polymer precipitate was collected by suction filtration and dried at room temperature to obtain poly(methyl methacrylate) (yield
10 64.3%).

GPC analysis [with reference to the molecular weight of an authentic sample of poly(methyl methacrylate)] revealed M_n 14000 and PD=1.10.

Example 8

15 Along with 1.001 g (10 mmoles) of methyl methacrylate (same as above), 30.18 mg (0.10 mmole) of the compound prepared in Preparation Example 3, 8.2 mg (0.05 mmole) of AIBN (same as above) and 18.5 mg (0.05 mmole) of the compound prepared in Preparation Example 5 were placed into a glove
20 box with the inside air replaced by nitrogen, followed by stirring at 60 °C for 2 hours. After the completion of the reaction, the reaction mixture was dissolved in 5 ml of chloroform, and the solution was then poured into 200 ml of hexane which was being stirred. The resulting polymer
25 precipitate was collected by suction filtration and dried at room temperature to obtain poly(methyl methacrylate) (yield 61.8%).

GPC analysis [with reference to the molecular weight of

an authentic sample of poly(methyl methacrylate)] revealed Mn 14800 and PD=1.17.

[EFFECT OF THE INVENTION]

The invention provides a process for preparing living
5 radical polymers which realizes precision control of
molecular weights and molecular weight distributions under
mild conditions.

Particularly, in the present invention, it is possible
to prepare living radical polymers having more precise
10 molecular weight and molecular weight distributions
($PD=M_w/M_n$) under mild conditions, even when not only styrene
but a vinyl monomer other than styrene such as a
(meth)acrylate ester, etc. is used.

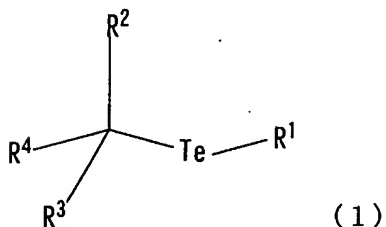
The living radical polymers obtained by the
15 polymerization process of the invention readily permit
conversion of terminal groups to other functional groups, are
useful for preparing macromonomers and useful as crosslinking
sites and are usable as compatibilizing agents and as
materials for block polymers.

[DOCUMENT NAME] ABSTRACT OF THE DISCLOSURE

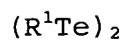
[ABSTRACT]

[PROBLEM] The present invention provides a process for producing a living radical polymer by polymerizing a vinyl monomer with use of an organotellurium compound represented by the formula (1), an azo type polymerization initiator and a ditelluride compound represented by the formula (2), the process making possible to prepare living radical polymers having more precise molecular weight and molecular weight distributions (PD=Mw/Mn) under mild conditions, even when not only styrene but a vinyl monomer other than styrene such as a (meth)acrylate ester, etc. is used; and the polymer.

[SOLVING MEANS] A process for producing a living radical polymer characterized in that a vinyl monomer is polymerized with use of an organotellurium compound represented by the formula (1), an azo type polymerization initiator and a ditelluride compound represented by the formula (2), and the living radical polymer obtainable by the process



wherein R^1 is C_1 - C_8 alkyl, aryl, substituted aryl or an aromatic heterocyclic group, R^2 and R^3 are each a hydrogen atom or C_1 - C_8 alkyl, and R^4 is aryl, substituted aryl, an aromatic heterocyclic group, oxycarbonyl or cyano



(2)

wherein R^1 is the same as above.

[SELECTED DRAWING] None